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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/889,078	07/11/2001	Mark Gilbert Benz	RD-25877	7997

7590 08/11/2005

General Electric Company
CRD Patent Docket Rm 4A59
P O Box 8
Building K-1 Salamone
Schnectady, NY 12301

EXAMINER	
MCNELIS, KATHLEEN A	
ART UNIT	PAPER NUMBER
1742	

DATE MAILED: 08/11/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

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PTO-90C (Rev. 10/03)

Office Action Summary	Application No.	Applicant(s)	
	09/889,078	BENZ ET AL.	
	Examiner	Art Unit	
	Kathleen A. McNelis	1742	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on 5/27/2005.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) 1-5 and 7-17 is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) 1-5 and 7-17 is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.
5) ☐ Notice of Informal Patent Application (PTO-152)
6) ☐ Other: _____.

CLAIMS STATUS

Claim 6 was cancelled. Claims 1-5 and 7-17 remain for examination, wherein claims 1, 5 and 7 are amended. Claims 12-17 were not addressed in the first office action, but have been examined and are addressed in the following detailed action.

EXAMINER'S COMMENTS

There appears to be a typographical error on claim number 17: "...a partial pressure of nitrogen in the flux, below the partial pressure of nitrogen in the flux below the partial pressure of nitrogen in the inclusion." Examiner has interpreted this to mean: "...a partial pressure of nitrogen in the flux, below the partial pressure of nitrogen in the inclusion."

DETAILED ACTION

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

The factual inquiries set forth in *Graham* v. *John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of

the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

Claims 1-5, 11-12 and 16 are rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al. (1994; US 5,332,197) in view of Choudhury et al. (US 5,234,486).

With respect to claims 1-4, Benz et al. (1994) discloses a method for the electroslag refining of titanium base alloys to achieve a low nitrogen content, the slag used will be a slag containing calcium fluoride or similar fluoride conventionally used with a particular titanium base metal in the conventional electroslag refining thereof (col. 6, lines 40-49).

Benz et al. (1994) does not specifically disclose the addition of dissolved calcium metal in the slag composition. Choudhury et al. discloses a method for remelting reactive metals, including titanium, by electroslag remelting in an inert gas atmosphere. In the method disclosed by Choudhury et al., calcium metal is added to purify the reactive metal (titanium) when melted. Choudhury et al. discloses equilibrium equations for the reaction of calcium metal with oxygen to produce CaO, and nitrogen to produce Ca_3N_2, which are then retained by the calcium fluoride slag (col 1. line 31 to col. 2 line 6). It would have been obvious to one of ordinary skill in the art at the time the invention

was made to add calcium metal to the slag of Benz et al. (1994), in order to reduce the amount of reactive oxygen and nitrogen in the flux and produce higher purity titanium as disclosed by Choudhury et al.

Benz et al. (1994) does not explicitly disclose the claimed sequence of steps for electroslag refining, however FIG 2 shows that the bottom surface of ingot 24 is melted (col. 11, lines 40-46); and that one can control the rate of melting by the level of refining power supplied to the vessel (col. 11 lines 47 to col. 12 line 2), and that the nitrogen present in the refined titanium is minimized (col. 12, lines 8-17). This process, as modified in view of Chourdhury to add calcium metal, is equivalent to the claimed process, although the exact words are not used, since melting titanium to reduce the nitrogen content with calcium fluoride and calcium metal is used in both methods.

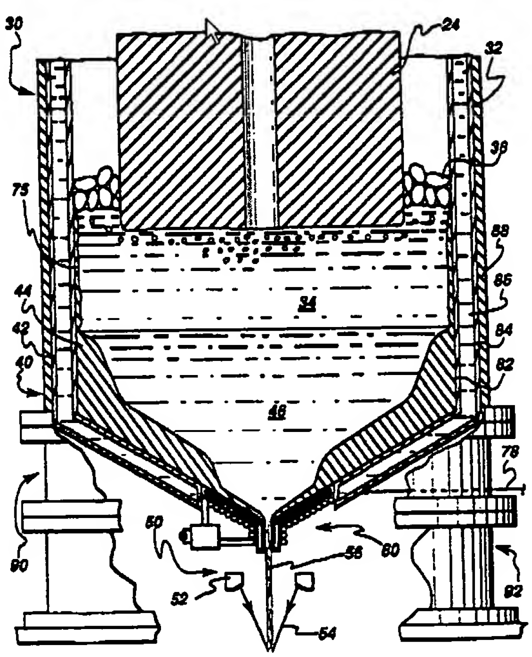

FIG. 2

With respect to amended claim 5, Benz et al. (1994) does not address additions of calcium oxide to the flux. Choudhury et al. discloses that it is beneficial to add calcium oxide to a flux formed of fluorspar (calcium fluoride), because the fluorspar has a low electrical resistance and would require higher power to heat than if calcium oxide is also added. Further, the calcium oxide is not reactive with titanium, and may be used to refine titanium alloys (col. 2, lines 6-17). It would have been obvious to one of ordinary skill in the art at the time the invention was made to add calcium oxides to the flux described in Benz et al. (1994) to reduce the electrical power required for heating, as disclosed in Choudhury et al.

With respect to claims 11 and 12, Benz et al. (1994) teaches that an inert gas, such as helium or argon, is circulated throughout the apparatus (col. 12, lines 56-68). Choudhury et al. discloses that the remelting of reactive metals is done with an inert gas atmosphere over the slag bath (col. 1, lines 27-50) to prevent oxidation, and that argon has proven most advantageous (col.2, lines 15-20). It would have been obvious to one of ordinary skill in the art at the time the invention was made to contain the flux and electrode disclosed in Benz et al. (1994) within an inert atmosphere to prevent oxidation as disclosed in Choudhury et al., and for that gas to be selected from the group of argon, neon, helium, hydrogen or mixtures thereof, since Choudhury et al. indicate that argon is most advantageous to purify reactive metals during remelting.

With respect to product claim 16, Since Benz et al. (1994) in view of Choudhury et. al., teaches a process similar to that of instant claim 1, the article made by the instant claim

1 would not be patentable over the article made by Benz et al. (1994) in view of Choudhury et al.

Amended claim 7 is rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994) in view of Choudhury et. al. as applied to claim 1 above, and in further view of Duckworth, et. al. in "Electro-slag Remelting", pages 47 to 50.

Benz et al. (1994) discloses a method for refining titanium in a calcium fluoride flux, but do not teach the addition of calcium metal to the flux. Choudhury et al. discloses the beneficial addition of calcium metal to the flux for titanium purification, but does not address the quantity of the addition. Duckworth et al. lists metals (including calcium) as minor components that may be added to slag for deoxidation, and discloses a composition of less than 10% for the metal addition (pages 47-50). Duckworth et al.'s disclosed range of less than 10% calcium in the slag overlaps the claimed range of from 1 to 4.5 weight % calcium. It has been well settled that where the applied prior art teaches a range of compositions or properties overlapping a claimed range, motivation to select a particular range or value within the range disclosed by the prior art would have been a modification obvious to one of ordinary skill in the art at the time the invention was made. See MPEP 2144.05. It would have been obvious to one of ordinary skill in the art at the time the invention was made to have added calcium to the flux of Benz et al. (1994) to benefit from the removal of reactive oxygen and nitrogen from the flux as disclosed by Choudhury et. al. Further, it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added to the

flux used in Benz et. al (1994) in view of Choudhury et al., a calcium metal composition in the flux of between 1 and 4.5%, selected from the range of less than 10% disclosed, because Duckworth et. al. teach that the whole range of addition up to 10% is beneficial for deoxidation.

Claim 8 is rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994; US 5,332,197) in view of Choudhury et al (US 5,234,486) as applied to claim 1 above, and in further view of Curtis et al (US 4,067,734).

Benz et al. does not explicitly disclose treating alpha-beta titanium, but such titanium alloy is conventional as evidenced by Curtis et al which discloses alpha-beta phase titanium alloys with no more than 0.05% nitrogen (col. 17, lines 33-40). It would have been obvious to one of ordinary skill in the art at the time the invention was made to apply the Benz et al.(1994) process in view of Choudhury et al., to refine a alpha-beta titanium alloy, as disclosed by Curtis et al.

Claims 9 and 10 are rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994; US 5,332,197) in view of Choudhury et al (US 5,234,486) as applied to claim 1 above and in further view of Duckworth, et. al.

In the method of Benz et al. (1994), resistance heating is used to melt the titanium electrode, however the operating process temperatures are not disclosed. Duckworth et. al. teaches that in order to melt the metal electrode, the slag must be fully liquid and at a temperature in excess of the liquidus of the metal being melted. The temperature ultimately reached in a slag bath is a function of the resistance of the slag bath and of the current passing through the slag bath (pp.17-18). Choudhury et al.

discloses that temperatures of above 1600 °C were reached in heating a calcium fluoride/calcium metal slag (col. 1, lines 38-49). The claimed temperatures of "above about 1500 °C" and "above about 1650 °C" overlap with the temperature range of over 1600 °C disclosed by Choudhury et al. as the operating temperature of the high-purity fluorspar slag process. It would have been obvious to one of ordinary skill in the art at the time the invention was made to use resistance heating to reach temperatures of above about 1500 °C or above about 1650 °C to melt the slag used in the Benz et. al. (1994) process in view of Choudhury et al., in order to ensure that the slag was fully liquid and above the liquidus of the metal electrode as taught by Duckworth et. al.

Claim 13 is rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994) in view of Choudhury et. al. as applied to claim 1 above, and in further view of Parsons (US 3,507,968).

Benz et. al (1994) does not specify that stirring occurs in the claimed process, however stirring by induced magnetic field is an inherent property of an electroslag furnace, as described in Parsons (col. 14 lines 60-65), and is beneficial for preventing segregation in the resulting product. It would have been obvious to a person of ordinary skill in the art at the time the invention was made to do nothing to prevent the inherent stirring in the apparatus of Benz et al. (1994) in view of Choudhury et al., thus receiving benefit of a product with superior morphology as disclosed by Parsons.

Claim 14 is rejected as rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994) in view of Choudhury et. al. as applied to claim 1 above.

Benz et al. (1994) claims a means for maintaining low partial pressure of nitrogen in the flux (col. 14, lines 3-7) and zero partial pressure (col. 14, lines 46 to 48). The claimed range of 10^{-12} to 10^{-15} atmospheres is within the range claimed in Benz et al. (1994) of between zero and "low" partial pressure. It would have been obvious to a person of ordinary skill in the art at the time the invention was made to achieve a partial pressure of nitrogen in the flux of between 10^{-12} to 10^{-15} atmospheres, since Benz et al. (1994) in view of Choudhury et al. indicates that a "low" nitrogen content in the flux is beneficial for removal of nitrogen from titanium.

Claim 15 is rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al (1994) in view of Choudhury et. al. as applied to claim 1 above and in further view of Duckworth et al.

Choudhury et. al. describe a method for titanium purification wherein high purity calcium fluoride slag is used, with calcium metal additive under an inert gas atmosphere to eliminate or minimize the oxygen content in the slag. Choudhury et. al. does not disclose the actual oxygen content of the slag. Duckworth et al. (p. 19) indicates that fluoride slags are "oxygen free." The claimed oxygen partial pressure of between 10^{-20} to 10^{-25} atmospheres is equivalent Duckworth et al.'s use of the term "oxygen free." It would be obvious to one of ordinary skill in the art at the time the invention was made to maintain the partial pressure of oxygen in the range of between 10^{-20} to 10^{-25} atmospheres in the Benz et. al. (1994) apparatus in view of Choudhury et al., as being essentially "oxygen free", thus minimizing the oxidation of the titanium as taught by Choudhury et. al.

Claim 17 is rejected under 35 U.S.C. 103(a) as being unpatentable over Benz et al. (1994; US 5,332,197) in view of Choudhury et al. (US 5,234,486) and in further view of Duckworth et al. and Snow (US 3,469,968).

Benz et al. discloses an electroslag remelting method to refine titanium alloys by heating in a non-oxidizing atmosphere a calcium halide flux (col. 6, lines 40-49). Benz et al. does not state the specific process steps for melting the electrode, however, FIG 2 (see above) shows that the bottom surface of ingot 24 is melted (col. 11, lines 40-46); and that one can control the rate of melting by the level of refining power supplied to the vessel (col. 11 lines 47 to col. 12 line 2), and that the nitrogen present in the refined titanium is minimized (col. 12, lines 8-17). Benz et al. (1994) discloses a method for recirculation and purification of the inert gas while the process is in operation to remove nitrogen (col. 12, lines 18-68). The purpose of the recirculation system is to treat the gas to remove nitrogen, which is described as beneficial as it reduces the partial pressure of nitrogen in the inert gas of the slag (col. 13, lines 1-10). This process will have the effect of maintaining the partial pressure of nitrogen in the flux at a lower partial pressure than in the inclusion.

Benz et al. (1994) does not specifically disclose the addition of calcium metal to the slag. Duckworth et al. lists metals (including calcium) as minor components that may be added to slag for deoxidation, and discloses a composition of less than 10% for the metal addition (pages 47-50). Duckworth et al.'s disclosed range of less than 10% calcium in the slag overlaps the claimed range of from 1 to 4.5 weight % calcium. It would have been obvious to one of ordinary skill in the art at the time the invention was

made to have used a calcium metal composition in the flux of between 1 and 4.5% in the process disclosed by Benz et al. (1994) in view of Choudhury et. al.; selecting the composition of 1 to 4.5 wt% from the range of less than 10% disclosed by Duckworth et al., because Duckworth et al. teaches that that the whole range of addition is beneficial for deoxidation of the slag.

Benz et al. (1994) does not disclose the operating temperature of the electroslag process. The claimed temperatures of "above about 1600 °C" is the same as the temperature range of over 1600 °C disclosed by Choudhury et al. It would have been obvious to one of ordinary skill in the art at the time the invention was made to heat the flux in the process of Benz et al. (1994) to above 1600 °C as disclosed in Choudhury et al.'s method for titanium purification in order to liquidfy the slag bath and melt the titanium electrode, as taught by Duckworth et al.

Benz et al. (1994) does not specify that alternating current be applied to the electrode, however Snow discloses a method for electroslag melting wherein alternating current is applied to an electrode which then melts under a cover of molten flux. Snow discloses that alternating current is selected over direct current because of faster more efficient melting (col. 2, lines 4-68). It would have been obvious to one of ordinary skill in the art to use alternating current in the method of Benz et al. (1994) in view of Choudhury et al. to achieve faster and more efficient melting of flux and electrode as described in Snow.

Response to Arguments

Applicant's arguments filed on May 25, 2005 with respect to claims 1-11 have been considered but are not persuasive.

With respect to amended claim 1, and claims depending therefrom, two additional references have been cited which specifically relate to the addition of calcium metal to a calcium fluoride flux (slag) for purification of a metal electrode in an electroslag process. Choudhury et al. (US 5,234,486) discloses the benefit of adding calcium metal to the slag in purification of titanium, as the calcium reacts with nitrogen and oxygen and binds them in the slag. Duckworth et al. ("Electro-slag Refining, Chapman and Hall Ltd, first published 1969) discloses the addition of alkali earth metals, including calcium to act as deoxidizers in a slag, and gives an addition range of less than 10%. The reduction of partial pressure is a result of a lower free oxygen and nitrogen in the flux. While Choudhury and Duckworth do not specifically state that the partial pressures of nitrogen and oxygen are reduced, this would be a result of the addition of calcium metal to the slag. It would have been obvious to one of ordinary skill in the art at the time the invention was made to add calcium metal to the flux of Benz et. al. (US 5,332,197) to react with nitrogen and oxygen in the flux, thus producing titanium of higher purity as disclosed in Choudhury.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Kathleen A. McNelis whose telephone number is 571-272-3554. The examiner can normally be reached on M-F 8:00 AM to 4:30 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Roy King can be reached on 571-272-1244. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

ROY KING
SUPERVISORY PATENT EXAMINER
TECHNOLOGY CENTER 1700

Notice of References Cited	Application/Control No. 09/889,078	Applicant(s)/Patent Under Reexamination BENZ ET AL.	
	Examiner Kathleen A. McNelis	Art Unit 1742	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-5,332,197	07-1994	Benz et al.	266/201
	B	US-5,234,486	08-1993	Choudhury et al.	75/10.26
	C	US-4,067,734	01-1978	Curtis et al.	148/421
	D	US-3,507,968	04-1970	PARSONS ROBERT C	373/47
	E	US-3,469,968	09-1969	SNOW KARL S	164/492
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
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	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Duckworth, W.E. and Hoyle, G., Electro-slag Refining, Chapman and Hall Ltd, first published 1969, USPTO receipt date Feb 2, 1971.
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Electro-slag Refining

W. E. DUCKWORTH
M.A., Ph.D., F.I.M., F.I.S., F.Inst.P.
and
G. HOYLE
B.Sc., F.I.M.

PATENT OFFICE
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11 NEW FETTER LANE LONDON E.C.4

3

The Physical and Chemical Properties of Slag and the Principles of Slag Selection

THE FUNCTION OF THE SLAG

The two most important functions of the slag layer are that it is the main source of heat and the principal means by which chemical composition is controlled.

The slag layer is the element of the electrical circuit between the transformer and the furnace which has the greatest resistivity, and hence is the part of the circuit most responsible for conversion of electrical energy into heat. If the slag has insufficient resistivity at the required operating temperature it will be very difficult to maintain satisfactory melting conditions.

The slag is the medium in which inclusions in the metal are removed by chemical reaction or dissolution and where the necessary adjustment of oxygen, sulphur, and other elements is achieved. If the slag is insufficiently reactive, then adequate cleanliness will not be obtained; if it is too reactive elements which should be retained will be removed.

The slag also performs a number of ancillary functions. By freezing on the mould wall it prevents direct contact between molten metal and the mould material, thus insulating the metal electrically and thermally from the mould and also helping to promote a smooth ingot surface. It protects the molten metal from direct atmospheric oxidation. It provides a heat reservoir above the molten metal which prevents piping and internal shrinkage. It acts as an agency by which manipulation not only of chemical composition but also of ingot structure can be achieved.

There is also the possibility of correcting the composition of out-of-specification metal by making additions during melting. Additionally grain size and shape can be controlled by both chemical and physical means.

PRINCIPLES OF SLAG SELECTION

For melting to take place in the ESR process it is necessary that the 'slag' be wholly liquid and be at a temperature in excess of the melting point (liquidus temperature) of the metal being melted.

The temperature attained in the slag bath is essentially a function of the *resistance* of the slag bath and of the current passing through that slag bath. The potential (20–50 volts) need only be sufficient to drive that current. Too high a potential, by causing arcing on the surface of the slag bath, can be detrimental to successful refining by promoting high oxidative losses from the metal.

The temperature attained in the slag bath, however, is not only dependent on the rate at which heat is generated but also on the rate at which heat is extracted. Heat is extracted by conduction, convection, radiation, and latent heat of fusion of metal. Of these the conductive losses to the cooling water via the mould walls and the baseplate are the most important.

The slag components must be stable at the process operating temperature, and they are therefore selected primarily on account of their *low vapour pressure*. Additionally they have to be capable, at process temperatures, of being able to refine the metal without themselves introducing serious deleterious contaminants.

Slags having liquidus temperatures at, below, or above the liquidus temperature of the metal can be used.

If the liquidus temperature of the slag is at or below that of the metal, then only sufficient energy (heat or electrical) to raise the temperature of the slag above the liquidus temperature of the metal need be applied. However, if the liquidus temperature of the slag is greater than that of the metal the amount of energy that need be applied has to be sufficient to raise the temperature of the slag to above the liquidus temperature of the slag.

The choice of a slag composition having a liquidus temperature at, or below, that of the metal makes most economic use of the energy.

However, if other factors, e.g. chemical, assume more importance than the economic utilization of energy, then a slag having a higher liquidus temperature than that of the metal may be used. For selection of appropriate slags it is therefore necessary to have a knowledge of the phase equilibria of the systems of interest in ESR. Other information required for the final selection are the physical properties: *vapour pressure*, *electrical conductivity*, *specific heat including latent heat of fusion and solution*, *viscosity*, *surface tension*, *and density*.

In the great majority of cases slags selected according to the principles and techniques described above will be satisfactory. In certain situations, however, very close control of particular elements may be necessary, and to achieve this fine degree of control it is necessary to understand the significant reactions occurring in the slag which control the properties of those elements in the slag and metal.

Phase equilibria

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(*ii*) Fluorides and oxi
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The most important slag

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the toxicity of fluorides
of increasing toxicity. I
baria (BaO) by pyrohyd

PHYSICAL PROPERTIES

Phase equilibria

The most important slag components are calcium fluoride, lime, magnesia, and alumina. Other important components include the fluorides of magnesium and barium and the oxides of barium, zirconium, and titanium. Chlorides have also been used when melting low-melting metals or alloys.

Using the slag components previously enumerated, slags may be classified as to whether they are composed of

(*i*) Fluorides only.
(*ii*) Fluorides and oxides.
(*iii*) Oxides only.

The most important slag systems involve fluoride–oxide mixtures.

Slag systems involving fluorides and chlorides are generally restricted in their application to the ESR of low-melting-point metals, such as copper and copper alloys. Systems used commonly contain the fluorides of calcium, magnesium, and barium.

Fluoride–oxide systems finding most universal applicability in ESR are those containing calcium fluoride and lime; calcium fluoride and alumina; calcium fluoride, lime, and aluminia; calcium fluoride, magnesia, and alumina.

FLUORIDE SYSTEMS

Fluorides alone or in combination can be used in the electro-slag refining process. Fluoride slags are oxygen free, have low melting points or liquidus temperatures, and because of their low electrical resistance give rise to relatively low process temperatures at the powers generally used. These properties make fluoride slags ideally suited for melting low-melting-point metals or alloys or those metals and alloys in which oxidation is to be minimal.

Calcium fluoride (CaF_2), magnesium fluoride (MgF_2), and barium fluoride (BaF_2), because of their low vapour pressures and therefore high-temperature stability, are the primary components of fluoride slags.

Of these three, calcium fluoride is the most important on account of a high-purity commercial grade being available in tonnage quantities at low cost (£22 per ton).* The fluorides of barium and magnesium are not readily available and are high in cost (£100 per ton).*

The order CaF_2–MgF_2-BaF_2 is the order of increasing water solubility. As the toxicity of fluorides is related to the solubility, the order given is also that of increasing toxicity. Barium fluoride is also hygroscopic and yields some baria (BaO) by pyrohydrolysis during fusion.

* Price ruling March 1969.

Sodium fluoride (NaF), aluminium fluoride (AlF_3), and cryolite (Na_3AlF_6) are generally unsatisfactory, as they boil and evolve copious fume at the temperatures commonly experienced in the process. The Russians, however, have reported successful melting of copper using a slag consisting of 80% calcium fluoride and 20% sodium fluoride and also calcium fluoride and barium chloride [1].

Single-component fluoride systems

(*i*) *CaF_2*. As previously explained, calcium fluoride or fluorspar is the most important constituent of fluoride slags.

The calcium fluoride used commercially is usually acid-grade low-sulphur fluorspar concentrates. A typical analysis of the material available in the U.K.* is as follows:

98% CaF_2	1% SiO_2	0·3% CaO
0·2% Al_2O_3	0·1% S	0·1% Pb

This material can be purified by prefusion usually in a graphite-lined induction or arc furnace. Prefusion removes hydrogen, sulphur, lead, and some silica. The removal of hydrogen is associated with an increase in lime (CaO) to about 2%, which can, on occasion, be as high as 5%. The elimination of hydrogen is according to the reaction

$$CaF_2 + H_2O = 2HF + CaO$$

The lime formed by pyrohydrolysis is sufficient to give desulphurization when metal or alloy is electro-slag refined through prefused fluorspar.

Pure calcium fluoride has a melting point of 1,418° C. but the commercial-grade spar has a liquidus temperature of about 1,380° C. As little as 0·5 wt-% lime CaO is sufficient to lower the liquidus temperature to 1,380° C.

Fluorspar on its own is difficult to use in the electro-slag process because of the difficulty in heating the slag bath to a high enough temperature. This difficulty is associated with its low electrical resistance (about 0·23 ohm cm at electro-slag refining temperatures, i.e. 1,650° C). However, when considering slags consisting of fluorides only, calcium fluoride slags are the easiest to work. This would suggest that of the fluorides, that of calcium has the higher resistance.

A variety of metals and alloys have been melted through fluorspar-only slags, and these include pure iron, mild steel (En32B and En42), ball-bearing steel (En31), 18/8 titanium stabilized stainless steel, and titanium. The titanium is reported as having been melted using a protective gas atmosphere [2–4] and preferably at a reduced pressure (0·5 torr) [3].

* Glebe Mines Ltd., Eyam, Derbyshire, England.

Consider electro-slag remelting pure iron through calcium fluoride using a cold slag start and a slag : metal weight ratio of 1:20.

In order to raise the temperature of 1 metric tonne of iron and 0·05 metric tonne of calcium fluoride from 298° K to 2,000° K requires $[(1{,}480 \times 10^6) + (2{,}449 \times 5 \times 10^4)] = 1{\cdot}602 \times 10^9$ joules (1,602 MJ). This is equivalent to 445·2 kWh.

Energy consumption of ESR process (pure iron being melted through calcium fluoride) is

445·2 kWh $tonne^{-1}$ of iron
452·3 kWh ton^{-1}
0·4452 kWh kg^{-1}
0·2019 kWh lb^{-1}

On a commercial ESR plant (Birlec) the energy consumption is 1,200 kWh ton^{-1}, then the efficiency of the process equals

$$\frac{\text{Work out}}{\text{Work in}} = \frac{452}{1{,}200} = 0{\cdot}377$$
$$= 37{\cdot}7\%.$$

SELECTION OF SLAG COMPONENTS

The selection of a slag is usually a two-stage process. The first step is to select the major components of the slag considering both types of component and the amounts of each. The major components of ESR slags are usually calcium fluoride, lime, magnesia, and alumina, these materials having high-temperature stability, i.e. low vapour-pressure, being readily available in a pure state and being of moderate cost. It is these components which determine the essential physical and chemical properties of the slag.

The second stage of selection, which may not always be necessary, consists in selecting the minor components of the slag. These minor components (less than 10%) include:

(*i*) Fluorides, e.g. magnesium and barium fluorides.
(*ii*) Stable oxides, e.g. barium and zirconium oxides.
(*iii*) Unstable oxides, e.g. titanium, silicon, iron, and manganese oxides.
(*iv*) Carbides, e.g. calcium carbide and graphite.
(*v*) Nitrides, silicides, and borides.
(*vi*) Metals, e.g. aluminium, calcium, titanium, misch metal.

The addition of minor components serves mainly to modify the chemical rather than the physical properties.

The factors to be considered when selecting slag compositions in the system CaF_2–CaO–MgO–Al_2O_3 are both economic and technical. Selection is made such that primary consideration is given to the economic require-

ments, only sufficient consideration being given to the technical requirements to ensure satisfactory quality and suitability for the particular application of the material to be refined by ESR.

THE ROLE OF CALCIUM FLUORIDE, LIME, MAGNESIA, AND ALUMINA

The role of the fluoride is to reduce the solidus and liquidus temperature, increase the electrical conductivity, and decrease the viscosity and surface tension of the slag.

The lime, however, is added primarily as a desulphurizing agent. It also reduces the electrical conductivity slightly.

The essential function of alumina is to increase the electrical resistance of the slag, and quite small amounts have a marked effect on slag electrical resistance. For instance, replacing 10% of calcium fluoride in pure calcium fluoride by alumina increases the electrical resistivity from 0·22 ohm cm to 0·26 ohm cm at 1,650° C. Replacing 30% of calcium fluoride by alumina increases the electrical resistivity still further from 0·22 ohm cm to 0·57 ohm cm at 1,650° C. A disadvantage of using alumina is that it can give rise to an increase in the oxygen content of the metal being remelted.

Replacing part of the alumina either by lime or magnesia reduces the risk of oxygen pick-up when using wholly fluorspar–alumina slags. The amount of magnesia should generally not exceed 15wt-% as a slag containing more than this is very difficult to operate. This is believed to be a result of increased slag viscosity.

ECONOMIC FACTORS INFLUENCING THE SELECTION

Ingot yield

Slag entrapment, centre looseness, piping, porosity, and hydrogen cracking all contribute to low yield. Slags containing little lime promote low ingot porosity and freedom from hydrogen cracking. Slags of low electrical resistance, i.e. those containing little alumina, give low melt rates, which reduce the risk of slag entrapment, centre-looseness, and piping.

Melt rate

High alumina content, i.e. high electrical resistance, promotes high melt rates and hence increased productivity (throughput).

Specific energy consumption

High alumina content, i.e. high electrical resistance, favours a low specific energy consumption kWh kg^{-1}.

Cost of slag materials

The ratio of costs of raw mate
keep the slag material costs
content high and the alumina

TECHNICAL FACTORS INFL

Soundness

Slag entrapment. Slow melt
contents reduce the risk of sla

Centre looseness and pipe. S
alumina contents reduce the

Porosity. Lime-poor slags
likely to cause porosity, than

Hydrogen cracking. Slags
hydrogen cracking than are
ingots of smaller cross-sectior

Cleanness. High lime con
content can cause an increase
not desirable.

Inclusion removal is favou
available for slag–metal reac
vertical solidification pattern
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Slow melt rates associated
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Selection of secondary or mi

EFFECT OF FLUORIDES

Small additions (5–10%) of
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EFFECT OF STABLE OXIDE

Small additions can be ma
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additions is to lower the l
potential of the slag. They
high cost.

Cost of slag materials

The ratio of costs of raw materials CaF_2–CaO–Al_2O_3 is 2·2:1:6·5. Hence, to keep the slag material costs minimal, it is advantageous to have the lime content high and the alumina content low.

TECHNICAL FACTORS INFLUENCING THE SELECTION

Soundness

Slag entrapment. Slow melt rates associated with low or moderate alumina contents reduce the risk of slag entrapment.

Centre looseness and pipe. Slow melt rates associated with low or moderate alumina contents reduce the risk of centre looseness and piping.

Porosity. Lime-poor slags are less prone to hydration, and hence are less likely to cause porosity, than lime-rich slags.

Hydrogen cracking. Slags of low lime content are less prone to cause hydrogen cracking than are lime-rich slags. Hydrogen only diffuses out of ingots of smaller cross-section, e.g. 8″ diameter, without causing cracking.

Cleanness. High lime content favours sulphur removal. High alumina content can cause an increase in metal aluminium and oxygen which is usually not desirable.

Inclusion removal is favoured by slow melt rates due to the increased time available for slag–metal reactions to take place. Slow melt rates also favour vertical solidification patterns which reduce the risk of residual non-metallic material enriched metal freezing in the centre of the ingot before the non-metallic material (oxides and sulphides) has had time to enter the slag phase. Slow melt rates associated with slags containing only small or moderate amounts of alumina therefore encourage the maximum degree of cleanness.

Selection of secondary or minor slag components

EFFECT OF FLUORIDES

Small additions (5–10%) of barium and magnesium fluorides serve to lower the liquidus temperature by a small amount.

EFFECT OF STABLE OXIDES

Small additions can be made of the stable oxides (those with low vapour pressures and having only one common valency state), such as the oxides of barium, zirconium, lanthanum, or the rare-earth metals. The effect of these additions is to lower the liquidus temperature and to reduce the oxygen potential of the slag. They are little used at present on account of their high cost.

EFFECT OF UNSTABLE OXIDES

The unstable oxides are those with relatively low negative free energy of formation ($-\Delta G^{\circ}$), such as silica (SiO_2), and variable valency of transition element oxides, such as the oxides of iron, manganese, titanium, etc. The presence of these oxides in anything but very small quantities (less than 5%) gives rise to an increase in metal oxygen content. However, iron oxide (2–4% FeO added as ferrous oxalate) or titania (25%) both inhibit the removal of sulphur from free-cutting steels.

EFFECT OF CARBIDES

The addition of small quantities (0·5–5%) of calcium carbide to calcium fluoride–lime slags has enabled low oxygen (less than 10 ppm) content and complete retention of the easily oxidizable elements, such as silicon and manganese, to be achieved when electro-slag remelting 1% C, 1·5% Cr bearing steel (En31, AISI 52100).

EFFECT OF SULPHIDES

Sulphides as iron or calcium sulphide have been added to calcium fluoride–alumina slags when it is desired to retain sulphur in free-cutting steels. Iron sulphide (FeS) is generally preferred in this application, as the product of its oxidation, iron oxide (FeO), inhibits desulphurization, whereas lime, the oxidation product of calcium sulphide, promotes desulphurization.

EFFECT OF METALS

Various slag deoxidation methods may be used to retain or lose an element in ESR metals. These slag deoxidants may be added either during slag fusion or continuously during remelting, the aim being to reduce the oxygen potential of the slag, and hence produce a remelted ingot of low oxygen content. Aluminium is a particularly suitable deoxidant, being cheap and readily available in wire form, which facilitates continuous feeding, using a wire feeder throughout a melt. Other suitable deoxidants are the usual ferro-alloys used in the metallurgical industry, but calcium, titanium, and misch metal are particularly good deoxidants.

EFFECT OF NITRIDES, SILICIDES, AND BORIDES

Little is known to date about the effects of adding nitrides, silicides, and borides to slags used in ESR. Nitrides have been added in order to retain a high nitrogen content during melting. However, the ESR process removes only a very small amount of nitrogen at the concentration at which it is usually found [6].

NEW CENTRAL FAX NUMBER

Effective July 15, 2005

On July 15, 2005, the Central FAX Number will change to **571-273-8300**. This new Central FAX Number is the result of relocating the Central FAX server to the Office's Alexandria, Virginia campus.

Most facsimile-transmitted patent application related correspondence is required to be sent to the Central FAX Number. To give customers time to adjust to the new Central FAX Number, faxes sent to the old number (703-872-9306) will be routed to the new number until September 15, 2005. After September 15, 2005, the old number will no longer be in service and **571-273-8300** will be the only facsimile number recognized for "centralized delivery".

CENTRALIZED DELIVERY POLICY: For patent related correspondence, hand carry deliveries must be made to the Customer Service Window (now located at the Randolph Building, 401 Dulany Street, Alexandria, VA 22314), and facsimile transmissions must be sent to the Central FAX number, unless an exception applies. For example, if the examiner has rejected claims in a regular U.S. patent application, and the reply to the examiner's Office action is desired to be transmitted by facsimile rather than mailed, the reply must be sent to the Central FAX Number.